

A SIMPLE METHOD FOR PREDICTING GAS HYDRATE FORMING CONDITIONS IN AQUEOUS MIXED ELECTROLYTE SOLUTIONS

Jafar Javanmardi and Mahmood Moshfeghian
Department of Chemical Engineering
Shiraz University, Shiraz, Iran
and

Robert N. Maddox
School of Chemical Engineering
Oklahoma State University, Stillwater, OK, USA

Key Words: Hydrate; Electrolyte; Gas

ABSTRACT:

A simple thermodynamic model is proposed for predicting hydrate forming conditions for natural gas components in the presence of single component or mixed electrolyte solutions. The parameters required for use of the model are developed and presented. The model is quite accurate with average deviations between calculated and experimental values of less than 0.5°C for systems not included in the model parameter determination.

INTRODUCTION:

Gas hydrates are a form of clathrate -- compounds in which guest molecules are entrapped in a cage lattice structure composed of host molecules. They were first discovered by Davy in 1810 who produced chlorine hydrate (24). Natural gas hydrates were first produced by Villard in 1888 (25). Hydrates of natural gas components are ice-like solid compounds that can form under temperature conditions 25°C (40°F) or more above the freezing point of water.

Several different hydrate structures are known. Most polar and some weakly polar gases form either a structure I or structure II hydrate. The hydrate formed depends primarily on the size of the guest molecule. Methane and ethane form structure I hydrates while propane and isobutane form structure II hydrates. Parrish and Prausnitz (18) reported the physical characteristics of structure I and II hydrates.

Gas hydrates are ice-like clathrate compounds that are solids. They can accumulate in low places or around valves and fittings causing gas gathering and flow lines to become clogged and shut off gas flow. This is a particular problem in cold weather when line temperatures are most likely to be in the hydrate forming range. Knowledge of hydrate forming conditions and ways of preventing hydrates from forming are important to the natural gas industry. These areas are well developed and reliable methods are available for both natural gas mixtures (Maddox, et al. 14) and gas mixtures with inhibitors present (Moshfeghian and Maddox, 16).

Salt solutions and brine are frequently produced along with natural gas. Also, hydrates have been suggested as one way of making sea water potable (Knox, et al., 12) and as a possible way of storing natural gas in salt pits (Miller and Strong, 15). Capabilities for predicting natural gas forming conditions in the presence of weak electrolytes need improvement. That is the justification for the work presented here.

APPROACH

The approach used to develop the procedure for estimating hydrate forming conditions for gases over electrolytes is similar to that used by Moshfeghian and Maddox (1990) for their work on inhibited water solutions. They predicted the conditions for hydrate formation over pure water and then calculated an adjustment, or change, in those conditions to account for the presence of the inhibitor.

In the present work the method of Holder, Corbin and Papadopoulos (1980) is used to calculate the conditions for hydrate formation over pure water, and equations are developed to adjust those conditions for the presence of electrolyte. Holder and co-workers used experimental measurements to generate chemical potential, enthalpy and heat capacity functions. No gas species dependent adjustable parameters are required.

THERMODYNAMIC MODEL

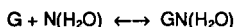
The equations used for predicting the influence of weak electrolyte solutions on natural gas hydrate forming conditions were developed from the work of van der Waals and Platteeuw, (23). The value of the Langmuir constant depends on temperature and potential energy function parameters and was evaluated using the mathematical expressions of Parrish and Prausnitz (18).

At equilibrium the chemical potential of water is equal in all phases present. If the free water is present as ice, none of the ice will be incorporated within the hydrate structure, and the chemical potential of the water in the hydrate will be equal to that of ice. If liquid water is present the free water and the water in the hydrate will have the same chemical potential.

The way in which the activity of water is evaluated depends on the components present in the system under consideration. If pure liquid water is present Holder, et al. (8) suggest that gas solubility in the water phase will be so slight that x_w , the mole fraction of water, may be used without creating significant error. If, on the other hand, water is present in an electrolyte solution with an appreciable concentration of salt present, the model suggested by Pitzer and Mayorga (22) can be used to estimate the activity of water in the electrolyte. Following Englezos and Bishnoi (5) and Tohidi, et al. (26) this work has used the Pitzer and Mayorga activity model for predicting conditions necessary for hydrate formation in the presence of electrolyte solutions.

In case there is more than one electrolyte present in the solution, the procedure proposed by Patwardhan and Kumar (19) is used to estimate the water activity.

Formation of hydrate from gas and liquid water molecules where G molecules of gas involve N molecules of water can be represented by the following chemical reaction:



For this representation Maddox, et al. (14) showed that the effect of a non electrolyte inhibitor on the hydrate temperature of a natural gas could be explained as:

$$\lambda n(a_w) = \frac{-\Delta H}{NR} \left(\frac{1}{T} - \frac{1}{T_w} \right) \quad (1)$$

The derivation of equation (1) is discussed in detail by Pieroen (21). The electrolyte can be treated as an "inhibitor" if the procedure developed is used for estimating electrolyte activities and other parameters. In this work $(\Delta H/NR)$, the enthalpy of hydrate formation per water molecule in the hydrate lattice in equation (1) is assumed to be a function of pressure and the ionic strength of the electrolyte solution and to take the following form:

$$\frac{\Delta H}{NR} = \frac{e_1 I^2}{1 + e_2 P + e_3 (\lambda n P)} \quad (2)$$

with e_1 , e_2 , e_3 and e_4 being adjustable parameters determined from experimental electrolyte solution hydrate data.

Experimental measurements of the hydrate temperature of methane (1, 2, 23) and ethane (6,26) in the presence of liquid water and electrolyte solutions and propane (8, 10, 13, 26) in the presence of ice, liquid water and electrolyte solution were used to evaluate the parameters in equation (2). The values are: $e_1 = 597.33$; $e_2 = -0.0409$; $e_3 = 0.0000227$; $e_4 = -0.0751$. These are global parameters that apply for any gas and any single or mixed electrolyte solution. They reproduce the measurements of Blanc and Tournier-Lasserre (1), Dholabhai, et al. (3), and Roo, et al. (23) for methane (CH_4) with an average absolute temperature deviation of 0.33°C; The experimental determinations by Englezos and Bishnoi (6) and Tohidi, et al. (26) for ethane are reproduced with an average absolute deviation of 0.56°C across all data points. Experimental data for propane by Englezos and Ngan (8), Holder and Godbole (10), Kubota, et al. (13), and Tohidi, et al. (26) are reproduced with an average absolute deviation for all propane data points of 0.35°C. A summary of these results is shown in Table 1.

CALCULATION PROCEDURE

Based on the discussion above a procedure for calculating the hydrate forming temperature and pressure for natural gas components in contact with water containing one or more electrolyte salts can be suggested. Assuming that the pressure is fixed and the hydrate forming temperature is required, the sequential steps in the procedure are:

1. Assume that the hydrate forming temperature in the presence of water with no electrolyte present is above 273.15K, the freezing point of water. If the hydrate temperature is lower than this, that fact will become evident and the assumed temperature can be changed. Use equations 3, 7 and 13 to evaluate T^0 .
2. Calculate the activity of water and $\Delta H/NR$.
3. Calculate the hydrate temperature in the presence of electrolyte.
4. If the temperature calculated in step 3 is greater than 273.15K, all is well; if it is lower than 273.15K return to step 1, assume the temperature is less than 273.15K, and repeat steps 2 and 3.

RESULTS

The procedure outlined has been used to predict hydrate forming conditions for carbon dioxide (CO₂) over electrolyte solutions. CO₂ is a different gas than light hydrocarbons in that it displays appreciable solubility in water, even at moderate pressures. There are cases in which gas solubility is high enough that the mole fraction of water in the water phase departs substantially from 1.0. The solubility of CO₂ in water can be expressed as:

$$x_{\text{CO}_2} = \left\{ \frac{f_{\text{CO}_2}^v}{(g_1 + g_2 T) \exp[(g_3 - P^*)/P^*]} \right\} \quad (3)$$

where:

$$\begin{aligned} g_1 &= -725919.22 \\ g_2 &= 2898.54 \\ g_3 &= 0.05127 \\ g_4 &= -0.11228 \end{aligned}$$

Calculations of CO₂ solubility using equation (3) match the experimental measurements of CO₂ solubility made by Stewart and Munjal (25) within an average absolute mole fraction CO₂ deviation of 0.00042 over temperatures from 259 to 281K and pressures from 1.0 to 4.25 MPa. Using equation (3) for CO₂ solubility in water and the hydrate prediction procedure developed here, the hydrate forming conditions for CO₂ over electrolyte solutions have been calculated and compared with experimental determinations made by Dholabhai, et al. (4), and Englezos (7). The results for CO₂ are summarized in Table 1. The 161 CO₂ data points show an average absolute temperature deviation of 0.46°C over the full temperature, electrolyte composition and pressure range of the data.

CONCLUSION

The model developed for predicting hydrate forming conditions in the presence of electrolyte solutions does an excellent job of reproducing experimental measurements. It also has the capability to make accurate predictions of hydrate formation in cases where the gas shows appreciable solubility in the water phase. It represents a significant step in predicting hydrate forming conditions for constituents of natural gas.

NOMENCLATURE

- a_w = activity of water
- a_w^0 = activity of water in the single salt solution defined by m_i^0
- A_ϕ = Debye-Hückel coefficient = 0.392 for water at 25°C
- β_0 = parameter in equation (10)
- β_1 = parameter in equation (10)
- β_2 = parameter in equation (10)
- C_{mj} = Langmuir constant
- C_p = specific heat, cal/g-mole-K
- f_λ = gas-phase fugacity of the λ th gas species
- h = molar enthalpy, cal/g-mole
- m = molality of electrolyte solution
- m_k = molality of electrolyte k in mixed electrolyte solution
- m_k^0 = molality of electrolyte k in a solution containing only electrolyte k and that has the same ionic strength as the mixed solution
- n = formula of electrolyte
- n_+ = number of positive ions in electrolyte formula
- n_- = number of negative ions in electrolyte formula
- nc = total number of components in gas phase
- R = gas constant, 1.987 cal/g-mole-K
- T = absolute temperature, K
- V = molar volume cm³/g-mole
- μ_w^H = chemical potential of water in the gas occupied lattice, cal/g-mole
- $\Delta\mu_w^H$ = change in chemical potential of water caused by hydrate formation, cal/g-mole
- μ_w^β = chemical potential of water in the unoccupied lattice, cal/g-mole
- μ_w^i = chemical potential of ice, cal/g-mole
- μ_w^λ = chemical potential of pure water, cal/g-mole
- θ_{mj} = fraction of the type m cavities which are occupied by a j -type gas molecule
- v_m = ratio of the number of type m cavities to the number of water molecules in the hydrate phase
- z = charge on ions in electrolyte formula

REFERENCES

1. Blanc, C., and J. Tournier-Lasserre, World Oil, November (1990).
2. Carson, D. B. and D. L. Katz, "Trans. AIME," 146, (1942).
3. Dholabhai, P. D., P. Englezos, N. Kalogerakis and P. R. Bishnoi, "Can. J. Chem. Eng.," 69, 800, (1991).
4. Dholabhai, P. D., N. Kalogerakis and P. R. Bishnoi, "J. Chem. Eng. Data," 38, (4), 650 (1993).
5. Englezos, P. and P. R. Bishnoi, "AIChE J.," 34, (10), 1718, (1988).
6. Englezos, P. and P. R. Bishnoi, "Ind. Eng. Chem. Res.," 30, (7), 1655, (1991).
7. Englezos, P., "Ind. Eng. Chem. Res.," 31, (9), 2232, (1992).
8. Englezos, P. and Y. T. Ngan, "J. Chem. Eng. Data," 38, (2), 250, (1993).
9. Holder, G. D. and G. Gorbin, "Ind. Eng. Chem. Fund.," 19, (3), 282, (1980).
10. Holder, G. D. and S. P. Godbole, "AIChE J.," 28, 930, (1982).
11. Jeffery, G. A. and R. R. McMullan, "Prog. Inorg. Chem.," 8, 43 (1967).
12. Knox, W. G., M. Hess, G. E. Jones and H. B. Smith, "Chem. Eng. Prog.," 57, (2), 66 (1961).
13. Kubota, H., K. Shimizu, Y. Tanaka and T. Makita, "J. Chem. Eng. Japan," 17, (4), 423, (1984).
14. Maddox, R. N., M. Moshfeghian, E. Lopez, C. H. Tu, A. Shariat and J. Flynn, Laurence Reid Gas Conditioning Conference, March 4-6, 1991.
15. Miller, B. and E. K. Strong, "Amer. Gas Assoc. Monthly," 28, (2), 63, (1946).
16. Moshfeghian, M. and R. N. Maddox, "Oil & Gas J.," 30, 78, (1993).
17. Moshfeghian, M. and R. N. Maddox, Annals of New York Academy of Science, 715, (1994).
18. Parrish, W. R. and J. M. Prausnitz, "Ind. Eng. Chem. Proc. Dev.," 11, 26 (1972).
19. Patwardhan, V. S. and A. Kumar, "AIChE J.," 32, (9), 1419, (1986).
20. Peng, D. Y. and D. B. Robinson, "Ind. Eng. Chem. Fund.," 59, (1976).
21. Pieroen, A. P., Recueil Trav. Chem., Vol. 74, 995-1002, (1955).
22. Pitzer, K. S. and G. Mayorga, "J. Phys. Chem.," 77, (19), 2300, (1973).
23. Roo, J. L., C. J. Peters, R. N. Lichenthaler and G. A. Diepen, "AIChE J.," 29, (4), 651, (1983).
24. Schroeder, W., Sammlung Chemischer & Chemisch-Technischer Vortäge, Ahren's, 1926.
25. Stewart, P. B. and P. Munjal, "J. Chem. Eng. Data," 15, (1), 67, (1970).
26. Tohidi, B., R. W. Burgass, A. Danesh and A. C. Todd, "SPE 26701," 255, (1993).
27. Van der Waals, J. H. and J. C. Platteeuw, "Advan. Chem. Phys.," 2, 1, (1959).
28. Villard, M., Comptes Rendus, 1888, 106, 1602.

Table 1

Component	Electrolyte Concentration mol/L			Temperature Range K	Pressure Range MPa	AATD* K
	NaCl	KCl	CaCl ₂			
CH ₄	0-5.43	0-1.57	0-1.07	261-281	2.39-92.0	0.33
C ₂ H ₆	0-4.28	0-1.88	0-1.59	265-283	0.50-2.0	0.56
C ₃ H ₈	0.4.27	0-3.35	0-1.61	248-278	0.1-0.54	0.35
CO ₂	0-4.29	0-2.36	0-2.24	259-281	1.0-4.23	0.46

* Average Absolute Temperature Deviation